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(54) Corrosion inhibiting functional fluid

(57) A functional fluid comprising an alcohol and corrosion inhibiting amounts of a saturated aliphatic dicarboxylic acid, such as adipic acid, or a water soluble salt thereof and a phosphate, molybdate, or mixture thereof is disclosed. The fluid is particularly useful as a non-corrosive antifreeze in the cooling system of an internal combustion engine.

GB 2 138 837 A

SPECIFICATION

C rr sion inhibiting functi nal fluid

This invention relates to the inhibition of corrosion of metal surfaces in contact with an alcohol-containing functional fluid and more particularly to the inhibition of metal corrosion due to contact with an aqueous alcohol antifreeze in the cooling system of an internal combustion engine.

In a variety of industrial processes, metal surfaces are contacted with alcohol-containing fluids that perform heat transfer, pressure transfer, freeze prevention, and various other functions. Such fluids include heating and cooling fluids, antifreeze and deicing fluids, and hydraulic fluids such as automotive brake fluids. The alcohols are not inherently corrosive to metals but are normally diluted with water to form the functional fluid or are exposed to moisture in use. Aeration of the aqueous fluid during use tends to induce corrosive conditions in the fluid which can become quite severe after prolonged use. In addition, rapid fluid flow or vibration can produce cavitation which occurs when flow conditions result in rapid formation and collapse of vapor pockets in the flowing liquid in regions of very low pressure. The resulting high localized shock forces erode protective metal oxide films and accelerate corrosion. Cavitation damage primarily occurs in components made of cast iron, aluminum and their alloys.

Alcohols such as ethylene glycol, propylene glycol and diethylene glycol are used as a nonvolatile, permanent-type antifreeze and high temperature transfer fluid in liquid-cooled automotive and stationary internal combustion engines to prevent freezing and overheating and damage to the engine water jacket. The most important property of an engine antifreeze formulation after heat transfer and freezing point depression characteristics is its ability to prevent corrosion in the cooling system. An automotive cooling system contains a variety of metals that are subject to corrosion and/or cavitation such as copper, solder, brass, steel, cast iron, and aluminum. Rust or other solid matter suspended in the coolant may cause erosion damage at points of high coolant velocity. The presence of oxygen and the high temperatures, pressures, and flow rates in automotive cooling systems increase the possibility of erosion and corrosion attack. Cavitation damage may also be a particular problem, for example, in the water pump, cylinder liners, crankcase, and radiator.

Various combinations of inorganic and organic inhibitors have been added to functional fluids to inhibit corrosion and cavitation and reduce damage to metallic surfaces. There are several difficulties in selecting an effective inhibitor combination for a given system. Each type of metal generally requires a separate corrosion inhibitor. For example, a given inhibitor may be effective to reduce corrosion of ferrous metals, but does not provide effective protection against corrosion of non-ferrous metal components of the system. Further, many conventional corrosion inhibitors are often ineffective in protecting cast iron and aluminium against cavitation or protect cast iron against cavitation but do not protect aluminum and aluminum alloys against corrosion. Some cast iron cavitation inhibitors may even cause increased corrosion of aluminum and aluminum alloys. Certain cavitation inhibitors may only be effective at high concentrations.

The functional fluid of the present invention comprises an alcohol and corrosion inhibiting amounts of a saturated aliphatic dicarboxylic acid or a water soluble salt thereof and a phosphate, a molybdate, or a mixture thereof. In the method of this invention, the corrosion of metallic surfaces, particularly those of the cooling system of an internal combustion engine, is inhibited by contacting the surfaces with the functional fluid. The invention provides excellent inhibition of corrosion of iron, aluminum, copper and zinc metals and their alloys under a wide range of conditions. The functional fluid is particularly effective as an antifreeze in an internal combustion engine in preventing corrosion of aluminum, cast iron, mild steel, yellow brass, silver solder, and copper components. Phosphate-containing inhibitors are particularly preferred for use in the antifreeze. The phosphate has buffering action, increases the reserve alkalinity, and is very effective in reducing cavitation of aluminum pumps. The addition of the acid or a mixture of the acid and the molybdate greatly improves the performance of the phosphate inhibitor. The molybdate salt also serves to increase the pH and the reserve alkalinity imparted to the cooling fluid prolongs the effective life of the inhibitor under severe conditions.

This invention employs a saturat d aliphatic dicarboxylic acid or a water soluble salt thereof. Suitable acids have the formula $HOOC(CH_2)_nCOOH$ wherein n is a whole number from 2 to 10. The acids are preferably water soluble but sparingly water soluble acids such as sebacic and higher acids may be used in the alcohol-based formulations f the present invention to provide a controlled level of inhibition. The acids includ succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, undecanoic, and dodecanoic acids. The acid is generally used in the free acid form but water soluble salts, including sparingly water soluble salts, may be used if desired. Inorganic salts of the acid such as its alkali metal, e.g., sodium or potassium, or ammonium salts or organic salts such as salts of low r amines, e.g., mono-, -di-, or triethanolamine are suitable.

The phosphates used in this invention are typically water soluble, inorganic phosphat s, such as mono, -di-, or tri-alkali metal phosphates. Suitable water soluble inorgaic phosphates includ phosphoric acid, disodium phosphate, sodium tripolyphosphate, sodium septaphosphate, tetrasodium pyrophosphat , sodium tripolyphosphate, sodium tetraphosphate, sodium hexametaphosphate, sodium decaphosphate or tetrapotassium pyrophosphate. The water soluble polyphosphates include molecularly dehydrated alkali metal phosphates having a ratio of alkali oxide to phosphorus pentoxide of from about 0.4 to 1 to about 2 to 1.

Any molybdate compound which will solubilize in the functional fluid to the extent necessary to make available a corrosion inhibiting amount of molybdate ions may be used in the present invention. An inorganic water soluble molybdate salt such as magnesium molybdate, ammonium molybdate, or an alkali metal molybdate, for example lithium molybdate, sodium molybdate, or potassium molybdate is preferred. Sodium molybdate and sodium molybdate dihydrate which are available commercially and are readily soluble in water are particularly preferred.

While it is possible to add each of the components separately to a functional fluid, it is generally more convenient to add them together in the form of a composition. The corrosium inhibiting composition used in the functional fluid of the present invention generally comprises from about 0.1 to about 100, preferably about 5 to about 75, parts by weight of the phosphate; from about 0.1 to about 100, preferably about 0.5 to about 10, parts by weight of the acid; and from about 0.1 to about 100, preferably about 0.5 to about 5, parts by weight of the molybdate.

Th composition preferably further comprises a water soluble nitrate, azole, silicate, or mixture thereof. These additional corrosion inhibitors generally comprise from about 0.1 to 100, and preferably comprise from about 1 to about 50, parts by weight of the composition.

Azoles are nitrogen-containing heterocyclic 5-membered ring compounds. Suitable water soluble azoles include thiazoles, isothiazoles, triazoles, pyrazoles, imidazoles, isooxazoles, and mixtures thereof as disclosed in U.S. Patents 2,618,608 and 2,742,369. Preferred azole compounds include 1,2,3-benzotriazole; 1,2,3-tolyltriazole; sodium 2-mercaptobenzothiazole; and sodium-2-mercaptobenzimidazole. Typically, the water soluble inorganic nitrate is sodium nitrate but other alkali metal nitrates and calcium nitrate are also suitable. An alkali metal silicate, such as sodium or potassium metasilicate, may be employed.

The compositions may include or be added to aqueous functional fluids containing other ingredients customarily employed in water treatment such as polymeric dispersants and other corrosion inhibitors. The compositions may be added to the fluid as dry powders and permitted to dissolve during use or may be used in the form of aqueous solutions. The solutions generally contain from about 0.1 to about 70 weight percent of the composition and preferably contain from about 1 to about 40 weight percent. The solutions can be made by adding the ingredients to water in any order.

Many different alcohols may be used in the functional fluids of this invention. Suitable alcohols are saturated aliphatic hydroxy compounds or mixtures thereof and include methyl, ethyl, propyl, and other monohydroxy alcohols as well as dihydroxy, trihydroxy, and other polyhydroxy alcohols such as ethylene glucol, propylene glycol, diethylene glucol, dipropylene glycol, other alkylene glycols, and glycerol. The alcohol is usually diluted with water to obtain a mixture of the desired freezing point or other functional properties. The alcohol generally comprises from about 10 to about 60 percent by weight of the fluid. A water soluble or miscible alcohol having about 1 to 5 carbon atoms such as methyl, ethyl, or propyl alcohols, ethylene glycol, or propylene glycol is preferably employed.

The amount of the corrosion inhibiting composition added to the functional fluid is an amount that is effective to inhibit corrosion and depends on the nature of the fluid to be treated. The composition generally is added to the fluid in an amount of from about 1 to about 10,000 parts per million (ppm) and preferably of from about 100 to about 9,000 parts per million of the fluid.

In the method of this invention, metallic surfaces are contacted with the functional fluid. The method may be employed with a wide variety of alcohol-containing functional fluids that contact metallic surfaces. Such fluids include heating and cooling fluids hydraulic fluids, and freeze prevention and deicing fluids. The fluids may be used, for example, in the internal combustion engines of automobiles and trucks, liquid-cooled aircraft engines, snow-melting systems, refrigeration systems, diesel locomotive engines, automatic sprinkler systems, brake and other hydraulic systems, heating systems, air conditioning systems, and deicing systems.

The invention is illustrated by the following examples in which all parts are by weight unless otherwise indicated.

EXAMPLES

A solid composition containing 64.66 parts of sodium phosphate, 6.47 parts of adipic acid, and 3.88 parts of sodium molybdate was prepared. The composition also contained 7.76 parts of sodium metasilicate, 7.76 parts of sodium nitrate, 6.47 parts of 2-mercaptobenzothiazole,

and 1.44 parts of 1,2,3-tolytriazole as additional corrosion inhibitors and 1.56 parts of a copolymer of sodium styrene sulfonate and maleic anhydrid as a dispersant. Compositions containing the same amount of the additional inhibitor and dispersant and one or more of the phosphate, adipic acid, and molybdate components of the present invention were also prepared.

The corrosion inhibiting properties of these compositions were evaluated in the ASTM-1384-70(1975) Corrosion Test for Engine Antifreezes In Glassware for high boiling antifreezes except that single instead of triplicate tests were conducted, some tests were conducted for one week instead of two weeks, and the tests were conducted by immersion in standard corrosive water (SCW in the following tables) and in a mixture of 50 parts by volume of ethylene glycol and standard corrosive water (50/50 in the following tables) instead of an antifreeze solution with a freezing point of $0 \pm 2°$. This standard corrosive water contained sufficient amounts of sodium sulfate, sodium chloride, and sodium bicarbonate in distilled water to provide 100 parts of each of sulfonate, chloride, and bicarbonate ions per million parts of water.

In the test, two inch by one inch (5 cm × 2.5 cm) coupons of the six metals commonly found in a cooling system were assembled in bundles to show not only chemical corrosion but any galvanic corrosion as well. The coupons were immersed in the heated test solutions which were aerated to acclerate any corrosion tendencies. After the test period, the metal coupons were cleaned and the corrosion was measured by weight loss.

The results of the test in milligrams of weight loss or weight gain in paretheses for each coupon after 1 week or 2 weeks as indicated and the components of the invention employed in the tests are shown in the following table.

GLASSWARE CORROSION TEST

SODIUM PHOSPHATE (One Week)

Fluid	*Dose, ppm*	*Copper*	*Silver Solder*	*Brass*	*Steel*	*Cast Iron*	*Cast Aluminum*
SCW	7780	6.2	22.3	7.6	5.9	29.5	4.3
SCW	3890	7.6	18.0	5.6	7.1	55.5	41.6
50/50	7780	5.8	0.2	6.7	2.0	7.6	(2.8)
50/50	3890	5.6	2.0	5.2	1.5	10.7	1.5

SODIUM PHOSPHATE AND ADIPIC ACID (One Week)

Fluid	*Dose, ppm*	*Copper*	*Silver Solder*	*Brass*	*Steel*	*Cast Iron*	*Cast Aluminum*
SCW	7788	2.8	(0.9)	0.7	1.0	2.0	1.8
SCW	3894	2.9	0.6	1.6	1.8	0.8	28.4

SODIUM PHOSPHATE AND SODIUM MOLYBDATE (One Week)

Fluid	*Dose, ppm*	*Copper*	*Silver Solder*	*Brass*	*Steel*	*Cast Iron*	*Cast Aluminum*
SCW	7088	2.1	0.3	0.6	(0.1)	0.4	1.5
SCW	3544	2.6	8.0	2.0	0.8	(0.4)	20.5

SODIUM PHOSPHATE, ADIPIC ACID AND SODIUM MOLYBDATE (One Week)

Fluid	*Dose, ppm*	*Copper*	*Silver Solder*	*Yellow Brass*	*Steel*	*Cast Iron*	*Cast Aluminum*
SCW	7713	7.7	16.5	9.1	1.2	4.0	(0.5)
SCW	3857	10.2	8.3	6.1	1.9	5.3	(1.7)
50/50	7713	5.5	(0.2)	4.0	0.5	1.1	(1.9)
50/50	3857	6.3	0.9	3.9	0.9	1.4	0.9

SODIUM PHOSPHATE, ADIPIC ACID, AND SODIUM MOLYBDATE (Two Weeks)

uid	Dose, ppm	Copper	Silver Solder	Yellow Brass	Steel	Cast Iron	Cast Aluminum
CW	7743	10.3	(1.3)	7.8	0.1	(0.5)	(0.9)
CW	3872	10.3	(1.0)	5.9	3.1	4.7	1.1

Th results demonstrate the excellent corrosion inhibition provided by the present invention.

In order to demonstrate more clearly the excellent corrosion inhibition provided by this invention, a simulated-service test was conducted. This test used an actual automobile radiator and wat r pump together with a cast-iron pot to simulate to engine block and the necessary hose connections and instrumentation. The pump was operated by an electric motor at the desir d speed. Metal coupons were joined together into bundles as in the ASTM Corrosion Test and the bundles were inserted in the pot and corrosion was measured by weight loss during the test period. Triplicate results after concurrent test periods of seven weeks are shown in the following table in milligrams of weight loss for each coupon.

SIMULATED SERVICE TEST
SODIUM PHOSPHATE, ADIPIC ACID, AND SODIUM MOLYBDATE (Seven Weeks)

Fluid	Dose ppm	Bundle No.	Copper	Silver Solder	Yellow Brass	Steel	Cast Iron	Cast Alumium
50/50	7713	1	1.5	1.7	0.9	2.0	5.4	0.7
50/50	7713	2	3.2	26.5	1.3	2.0	7.4	0.1
50/50	7713	3	1.3	2.1	1.5	1.9	9.7	1.1
Average			2.0	1.9	1.2	2.0	7.5	0.6

The composition again provided excellent corrosion inhibition in this test.

CLAIMS

1. A fluid comprising an alcohol, and, as corrosion inhibitor, a saturated aliphatic dicarboxylic acid or a water soluble salt thereof, and a phosphate or a molybdate or a mixture thereof.

2. A fluid according to claim 1 in which the dicarboxylic acid or salt is succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanoic acid, dodecanioc acid, a water soluble salt thereof, or a mixture thereof.

3. A fluid according to claim 1 or 2 in which the dicarboxylic acid or salt is adipic acid or a water soluble salt thereof.

4. A fluid according to any one of claims 1 to 3 comprising a mixture of a water soluble inorganic phosphate and a water soluble inorganic molybdate.

5. A fluid according to any one of claims 1 to 4 further comprising a water soluble nitrate, azole, or silicate, or a mixture thereof.

6. A fluid according to any one of claims 1 to 5 comprising from 0.1 to 100 parts by weight of the dicarboxylic acid or salt and from 0.1 to 100 parts by weight of the molybdate.

7. A fluid according to any one of claims 1 to 6 in which the molybdate is sodium molybdate and the dicarboxylic acid is adipic acid.

8. A fluid according to any one of claims 1 to 7 in which the alcohol is an alkylene glycol.

9. A non-corrosive antifreeze liquid according to any one of the preceding claims comprising an aqueous solution of ethylene glycol and a corrosion inhibitor comprising from 0.5 to 5 parts by weight of sodium molybdate, from 0.5 to 10 parts by weight of adipic acid, from 5 to 75 parts by weight of sodium phosphate, and from 1 to 50 parts by weight of a mixture comprising sodium nitrate, sodium silicate, sodium 2-mercaptobenzothiazole, and 1,2,3-tolyltriazole.

10. A fluid according to claim 1 substantially as hereinbefore described.

11. A method of inhibiting corrosion of a metallic surface in contact with a functional fluid which comprises contacting the surfaces with a fluid as claimed in any one of claims 1 to 10.

12. A method according to claim 11 in which the dicarboxylic acid or salt is succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanoic acid, dodecanoic acid, a water soluble salt thereof, or a mixture thereof.

13. A method according to claim 11 in which the dicarboxylic acid or salt is adipic acid or a water soluble salt thereof.

14. A m thod according to any one of claims 11 to 13 in which th fluid comprises a mixture of a water soluble inorganic phosphate and a water soluble inorganic molybdate.

15. A method according to any ne of claims 11 to 14 in which the fluid further compris s

a water soluble nitrate, azole or silicate, or a mixture thereof.

16. A method according to any one of claims 11 to 15 in which the fluid comprises from 0.1 to 100 parts by weight of the dicarboxylic acid or salt and from 0.1 to 100 parts by weight of the molybdate.

17. A method according to any one of claims 11 to 16 in which the molybdate is sodium molybdate and the dicarboxylic acid is adipic acid.

18. A method according to any one of claims 11 to 17 in which the alcohol is an alkylene glycol.

19. A method according to any one of claims 11 to 18 in which the corrosion inhibitor is present in the fluid in an amount of from 1 to 10,000 parts per million of the fluid.

20. A method according to any one of claims 11 to 19 of inhibiting corrosion of metallic surfaces of a cooling system of an internal combustion engine which comprises contacting the surfaces with an aqueous solution comprising ethylene glycol and a corrosion inhibitor comprising from 0.5 to 5 parts by weight of sodium molybdate, from 0.5 to 10 parts by weight of adipic acid, from 5 to 75 parts by weight of sodium phosphate, and from 1 to 50 parts by weight of a mixture comprising sodium nitrate, sodium silicate, sodium 2-mercaptobenzothiazole and 1,2,3-tolyltriazole.

21. A method according to claim 11 substantially as hereinbefore described.

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